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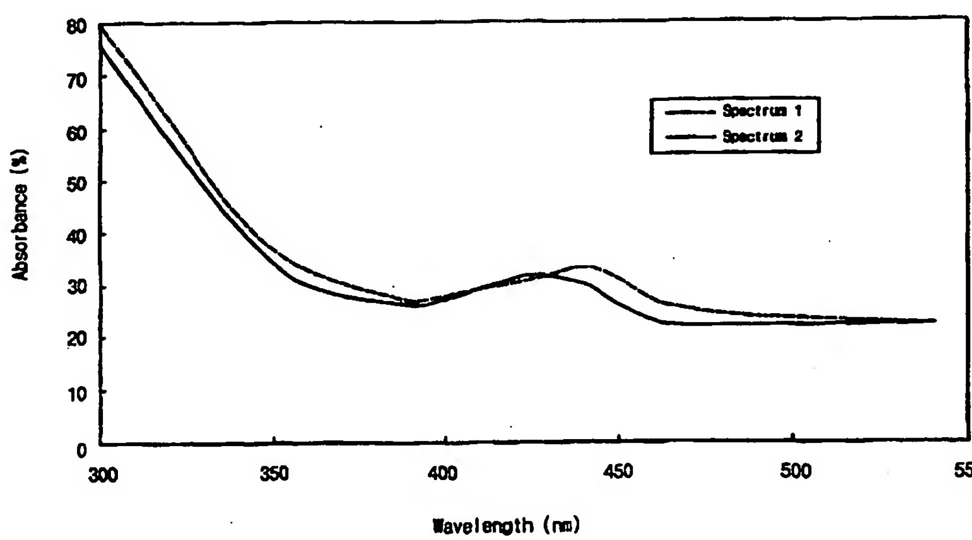

(57) Abstract

The present invention relates to a catalyst system for olefin polymerization and copolymerization and method using the catalyst system, and more specifically to method for preparing olefin polymers with high yield, which have high molecular weight and good physical properties, using conventional metallocene catalyst and cation activator represented by $M^{n+}(X^-)_{n-g}Z_g$ and alkylating agent instead of expensive methyl aluminoxane or boron-based cocatalyst.

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CATALYST SYSTEM FOR (CO)POLYMERIZATION OF OLEFINS AND PROCESS FOR THE PREPARATION OF OLEFIN (CO)POLYMERS USING THE CATALYST SYSTEM

Field of the Invention

The present invention relates to a catalyst system for polymerization and copolymerization of olefins and process for the preparation of olefin homo- or co- polymers using the catalyst system. More specifically, the present invention relates to a metallocene catalyst system and process using the catalyst system for producing, with high yield, olefin homo- or co- polymers such as ethylene-propylene rubber(EPR) and linear low density polyethylene(LLDPE), which have high molecular weight and good physical properties, without concurrent use of expensive cocatalysts such as methyl aluminoxane(hereinafter referred to as "MAO"), boron-based cocatalyst, etc.

Background Art

The stereospecificity of conventional Ziegler-Natta (Z.N) catalyst was controlled by coordinate unsaturation of active compounds for polymerization existing on the surface of solid. In the metallocene catalyst system, however, polymer having atactic(C2v symmetry), syndiotactic(Cs symmetry) or isotactic(C2 symmetry) structure can be prepared simply by changing symmetry of ligands. Homogeneous olefin copolymers having high random characteristics are also obtainable by employing the metallocene catalyst. Furthermore, the catalyst shows high activity towards olefins with bulky substituents, which makes it possible to prepare long chain branched polyethylene without relying on high pressure radical polymerization method. Metallocene catalyst exhibits good polymerization activity for some polar olefins or 1,3-diene, α, ω-diene as well as for cycloolefins such as cyclobutene, cyclopentene, norbornene. Generally, the metallocene catalyst comprises transition metal complex represented by the general formula (I).

$$(CpR_n)(CpR'_m)MQ_p \qquad (I)$$

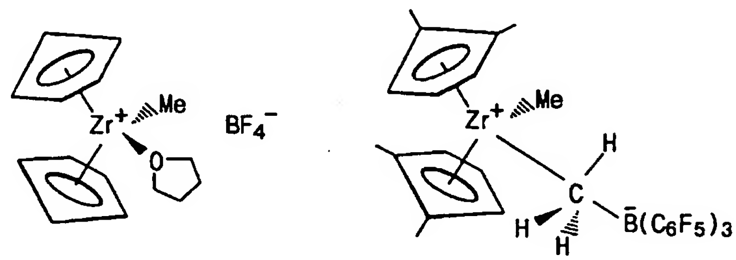
wherein, CpRn or CpR'm is a cyclopentadienyl, indenyl or fluorenyl which is unsubstituted or substituted with one or more alkyl, phosphine, amine, alkyl ether, or allyl ether groups; M is a transition metal from Group IVB ["CRC Handbook of Chemistry and Physics", 68th ed., 1987-1988] or VB of the Periodic Table of Elements; Q is alkyl, allyl, allyl alkyl, amide, alkoxy, halogen, sulphide, phosphide; n, m and p are $0 \leq n \leq 5$, $0 \leq m \leq 5$ and $1 \leq p \leq 4$, respectively.

The metallocene catalyst does not show catalystic activity by itself. Dr. Kaminsky et al. reported that the catalyst exhibited high activity for ethylene polymerization and could produce polymers having narrow molecular weight distribution when excess MAO was used together with. [H, Sinn, W. Kaminsky, H. J. Vollmer, R Woldt, Angew. Chem., 92, 296(1980), H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18, 99(1980), and W. Kaminsky, K. Külper, H. H. Brintzinger, F. R. W. P. Wild, Angew, Chem., Int. Ed. Engl. 24, 507(1987)] The catalyst system, however, is very costly because expensive MAO (approximately 400US$/kg) should be added 2,000-10,000 times more than the amount of the metallocene catalyst. And aluminum remnants in polymer products makes it difficult to analyze quantity of active compounds, reaction mechanism, etc. Thus, the catalyst system is disadvantages for industrial use.

Jordan et al. reported that $[Cp_2ZrMe(THF)^+BF_4^-]$ had ethylene polymerization activity, but it was very low [R. F. Jordan, C. S. Bajgur, R. Willett and B. Scott, J. Am. Chem. Soc., 108, 7410(1986)]. To increase its activity, it is required to form a complex wherein cationic metal center can interact with counter anion as weakly as possible, not involving molecular donation from donor such as THF. In case $RB(C_6F_5)_3^-$ employing fluorine as a counter anion is used, electrostatic interaction with cationic metal center can be weaken due to moderated negative charge of boron.

According to Marks et al, a complex wherein a methyl group of boron was weakly bonded to zirconium was formed when $CH_3B(C_6F_5)_3^-$ was used as a counter anion, and this complex made high active catalyst for olefin polymerization[X-Yang, C. L. Sterm, and

T. J. Marks, Angew. Chem. Int. Ed. Eng., 31, 1375(1992)]. The structure has been clarified based on a hydride complex obtainable by adding hydrogen to the complex.



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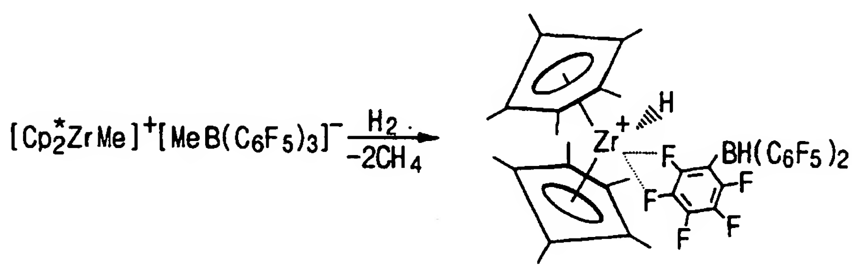


This structure shows that zirconium interacts with ortho- or metha-fluorines of a C_6F_5 ring. This complex is regarded as high active compound model produced by β-elimination during olefin polymerization, and also exhibits high activity for polymerization [3200kg PE/mol-Zr h atm, Mn = 1.545×10^5, Mw/Mn = 2.8, 320kg PP/mol-Zr h, Mw/Mn = 1.6].

However, conventional metallocene catalyst systems described above still require excess MAO or boron based cocatalyst that the catalyst systems are not suitable for commercial use. And aluminum remnant is found in polymer products. Therefore, it is keenly needed to develop a cocatalyst substituting for MAO. The present invention is directed to solve such problems in conventional catalyst systems.

Thus, it is an object of the present invention to provide a metallocene catalyst system and process using the catalyst system for producing olefin homo- or co- polymers having a high molecular

weight, with high yield, not employing MAO or boron-based cocatalyst. These characteristics of the present invention are advantageous in terms of industrial use, and it is also important considering the catalyst system as it is.

Brief Description of the Drawings

FIG. 1a is UV-Vis absorption spectrum in case of using rac-ethylene bis(indenyl)zirconium dichloride catalyst, and FIG. 1b is spectrum in case of adding magnesium perchlorate; and

FIG. 2a is DSC (Differential Scanning Calorimeter) spectrum of ethylene-octene copolymer obtained by using a metallocene catalyst bis(n-butylcyclopentadienyl)zirconium dichloride, and FIG. 2b is spectrum of polymer obtained by using Ziegler-Natta catalyst.

Disclosure of the Invention

To this end, the present invention provides a catalyst system for olefin polymerization and copolymerization comprising (A) at least one metallocene compound derived from a transition metal, (B) at least one cation activator as cocatalyst, and (C) at least one alkylating agent.

Further, the present invention provides a process for preparing copolymers such as ethylene-α-olefin copolymers such as ethylene-propylene copolymer, ethylene-1-octene copolymer, and ethylene-styrene copolymer, ethylene-diene copolymer or ethylene-cycloolefin copolymer as well as olefin homopolymers such as polyolefin, using the catalyst system.

Said component (A) is a metal selected from IIIB, IVB, VB, VIB, VIIB, VIIIB, IB or IIB Group of the Periodic Table of Elements, bonded to one or more functional group containing C, Si, N, P, As, Sb, O, S, Se, F, Cl, Br or I, and it is known per se.

Said component (B) is the compound represented by the following general formula, and also known per se.

$$M^{n+}(X^-)_{n-g}Z_g$$

wherein, $n = 1, 2, 3$ or 4, g is an integer such that $0 \leq g < n$; M

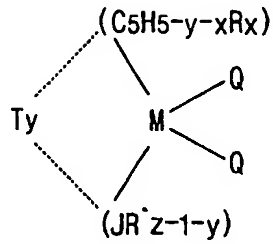
is a metal selected from IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIIIB, IB or IIB Group of the Periodic Table of Elements or an organic compound; X is an anion cluster comprising more than three elements, wherein one or more element is selected from the group consisting of O, S, N, F, Cl, Br and I; and Z is $H^{\cdot}$, or F, Cl, Br or I, which can form a coordinate bond with M.

Component (C) is an organometallic compound having hydrocarbyl group such as C_1-C_{20} alkyl, alkenyl, arylalkyl or allylalkyl, wherein said metal is selected from IA, IIA, IIB or IIIA Group of the Periodic Table of Elements, and also known per se.

The present invention is characterized in using the catalyst system comprising component (A), component (B), and component (C), appropriately blended, for preparing olefin homo- or co-polymers. Said component (B) and component (C) are cocatalysts for activating the metallocene catalyst (A). Therefore, the amount of each component added to the catalyst system should be enough to activate the component (A).

The molar ratio of component (A) to component (B) is 1 : 0.01 ~ 100, preferably 1 : 0.1 ~ 10, more preferably 1 : 1. And, the molar ratio of component (A) to component (C) is 1: 1 ~ 10,000, preferably 1 : 100 ~ 2,000.

Transition metal complexes which can be used as component (A) are dialkyl metallocene represented by general formula (I) ; bridged metallocene represented by formula R"(CpRn)(CpR'm)MQp [wherein, CpRn or CpR'm is cyclopentadienyl, indenyl or fluorenyl which is unsubstituted or substituted with one or more compounds selected from the group consisting of alkyl, phosphine, amine, alkyl ether, allyl ether; R" represents bridge between Cp rings, M is transition metal of Group IVB or VB of the periodic table, Q is alkyl, allyl, allyl alkyl, amide, alkoxy, halogen, sulfide, phosphide; and, n, m and p are respectively $0 \leq n \leq 4$, $0 \leq m \leq 4$ and $1 \leq p \leq 4$]; and monocyclopentadienyl IVB transition metal catalyst represented by following general formula.



wherein,

M is zirconium, Hafnium or titanium having the largest oxidation number (+4, d^0 complex);

($C_5H_{5-y-x}R_x$) is a cyclopentadienyl compound, herein X is 0, 1, 2, 3, 4 or 5 denoting the number of substituents, R is C_1-C_{20} hydrocarbyl radical whose hydrogen can be substituted with halogen, amino, phosphido, alkoxy radical, Lewis' acid group or radical having basic functional group;

(JR'_{z-1-y}) is a hetero atom ligand, herein J is a compound from Group VA whose coordination number is 3 or a compound from Group VIA whose coordination number is 2, preferably N, P, O, S and more preferably N; R′ is C_1-C_{20} hydrocarbyl radical whose hydrogen can be subsituted with halogen, amino, phosphido, alkoxy radical, Lewis' acid group or radical having basic functional group; z is coordination number of J, and y is 0 or 1;

Q is halogen, hydride, unsubstituted or substituted C_1-C_{20} hydrocarbyl, alkoxide, allyl oxide, amide, allyl amide, phosphide, allyl phosphide.

Such dialkyl metallocene described includes, for example, bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)hafnium diphenyl, bis(cyclopentadienyl)titanium dineopentyl, bis(cyclopentadienyl)zirconium dineopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)vanadium dimethyl.

Mono-alkyl or mono-allyl metallocene are, for example, bis(cyclopentadienyl)titanium methylchloride, bis(cyclopentadienyl)titanium ethylchloride, bis(cyclopentadienyl)titanium pentylchloride, bis(cyclopentadienyl)zirconium methylchloride, bis(cyclopentadienyl)zirconium ethylchloride, bis(cyclopentadienyl)zirconium phenylchloride, bis(cyclopentadienyl)titanium methlybromide, bis(cyclopentadienyl)titanium methyliodide, bis(cyclopentadienyl)titanium ethylbromide, bis(cyclopentadienyl)titanium ethyliodide, bis(cyclopentadienyl)titanium phenylbromide, bis(cyclopentadienyl)titanium phenyliodide, bis(cyclopentadienyl)zirconium methylbromide, bis(cyclopentadienyl)zirconium methyliodide, bis(cyclopentadienyl)zirconium ethylbromide, bis(cyclopentadienyl)zirconium ethyliodide, bis(cyclopentadienyl)zirconium phenylbromide, bis(cyclopentadienyl)zirconium phenyliodide.

Trialkyl metallocene are, for example, cyclopentadienyltitanium trimethyl, cyclopentadienylzirconiumtriphenyl, cyclopentadienyltitaniumtrineopentyl, cyclopentadienylzirconiumtrimethyl, cyclopentadienylhafniumtriphenyl, cyclopentadienylhafniumtrineopentyl, cyclopentadienylhafniumtrimethyl.

Dihalide metallocene are, for example, bis(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)zirconium dichloride.

Further, bridged metallocene descibed includes, for example, dimethylsilylbis(1-indenyl)zirconium dibromide, dimethylsilylbis(1-indenyl)zirconium diethyl, dimethylsilylbis(1-indenyl)zirconium dimethoxide, dimethylsilylbis(1-indenyl)zirconium dihydride, dimethylsilylbis(1-indenyl)zirconium chloride bromide, dimethylsilylbis(1-indenyl)zirconium chloride methoxide, dimethylsilylbis(1-indenyl)zirconium chloride methyl,

dimethylsilylbis(1-indenyl)zirconium chloride hydride,
dimethylsilyl(9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride,
dimethylsilyl(9-fluorenyl)(1-cyclopentadienyl)zirconium dimethyl,
dimethylsilyl(9-fluorenyl)(1-cyclopentadienyl)zirconium diethoxide,
dimethylsilylbis(9-fluorenyl)zirconium dichloride,
dimethylsilylbis(9-fluorenyl)zirconium dimethyl,
dimethylsilylbis(9-fluorenyl)zirconium diethoxide,
dimethylsilylbis(1-cyclopentadienyl)zirconium dichloride,
dimethylsilylbis(1-cyclopentadienyl)zirconium dimethyl,
dimethylsilylbis(1-cyclopentadienyl)zirconium diethoxide,
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dimethylsilyl(1-indenyl)(1-cyclopentadienyl)zirconium dichloride,
dimethylsilyl(1-indenyl)(1-cyclopentadienyl)zirconium dimethyl,
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dimethylsilyl(1-indenyl)(9-fluorenyl)zirconium dichloride,
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dimethylsilyl(1-indenyl)(9-fluorenyl)zirconium diethoxide,
dimethylsilyl(9-fluorenyl)(1-cyclopentadienyl)hafnium dichloride,
dimethylsilyl(9-fluorenyl)(1-cyclopentadienyl)hafnium dimethyl,
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dimethylsilyl(1-indenyl)(1-cyclopentadienyl)hafnium dichloride,
dimethylsilyl(1-indenyl)(1-cyclopentadienyl)hafnium dimethyl,
dimethylsilyl(1-indenyl)(1-cyclopentadienyl)hafnium diethoxide,

dimethylsilyl(1-indenyl)(9-fluorenyl)hafnium dichloride, dimethylsilyl(1-indenyl)(9-fluorenyl)hafnium dimethyl, dimethylsilyl(1-indenyl)(9-fluorenyl)hafnium diethoxide, 2,2-propyl bis(1-indenyl)zirconium dibromide, 2,2-propyl bis(1-indenyl)zirconium diethyl, 2,2-propyl bis(1-indenyl)zirconium dimethoxide, 2,2-propyl bis(1-indenyl)zirconium dihydride, 2,2-propyl bis(1-indenyl)zirconium chloride bromide, 2,2-propyl bis(1-indenyl)zirconium chloride methoxide, 2,2-propyl bis(1-indenyl)zirconium chloride methyl, 2,2-propyl bis(1-indenyl)zirconium chloride hydride, 2,2-propyl bis(trimethylcyclopentadienyl)zirconium dichloride, 2,2-propyl bis(5-dimethylamino-1-indenyl)zirconium dichloride, 2,2-propyl bis(6-dipropylamino-1-indenyl)zirconium dichloride, 2,2-propyl bis(4,7-bis(dimethylamino)-1-indenyl)zirconium dichloride, 2,2-propyl bis(5-diphenylphosphino-1-indenyl)zirconium dichloride, 2,2-propyl (1-methylamino-9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, 2,2-propyl (4-butylthio-9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, 2,2-propyl bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, 2,2-propyl bis(4-methyl-1-indenyl)zirconium dichloride, 2,2-propyl bis(5-methyl-1-indenyl)zirconium dichloride, 2,2-propyl bis(6-methyl-1-indenyl)zirconium dichloride, 2,2-propyl bis(7-methyl-1-indenyl)zirconium dichloride, 2,2-propyl bis(5-methoxy-1-indenyl)zirconium dichloride, 2,2-propyl bis(4,7-dimethoxy-1-indenyl)zirconium dichloride, 2,2-propyl bis(2,3-dimethyl-1-indenyl)zirconium dichloride, 2,2-propyl bis(4,7-dimethyl-1-indenyl)zirconium dichloride,

2,2-propyl (9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, 2,2-propyl (9-fluorenyl)(1-cyclopentadienyl)zirconium dimethyl, 2,2-propyl (9-fluorenyl)(1-cyclopentadienyl)zirconium diethoxide, 2,2-propyl bis(9-fluorenyl)zirconium dichloride, 2,2-propyl bis(9-fluorenyl)zirconium dimethyl, 2,2-propyl bis(9-fluorenyl)zirconium diethoxide, 2,2-propyl bis(1-indenyl)zirconium dichloride, 2,2-propyl bis(1-indenyl)zirconium dimethyl, 2,2-propyl bis(1-indenyl)zirconium diethoxide, 2,2-propyl (1-indenyl)(1-cyclopentadienyl)zirconium dichloride, 2,2-propyl (1-indenyl)(1-cyclopentadienyl)zirconium

dimethyl, 2,2-propyl (1-indenyl)(1-cyclopentadienyl)zirconium diethoxide, 2,2-propyl (1-indenyl)(9-fluorenyl)zirconium dichloride, 2,2-propyl (1-indenyl)(9-fluorenyl)zirconium dimethyl, 2,2-propyl (1-indenyl)(9-fluorenyl)zirconium diethoxide, 2,2-propyl (9-fluorenyl)(1-cyclopentadienyl)hafnium dichloride, 2,2-propyl (9-fluorenyl)(1-cyclopentadienyl)hafnium dimethyl, 2,2-propyl (9-fluorenyl)(1-cyclopentadienyl)hafnium diethoxide, 2,2-propyl bis(9-fluorenyl)hafnium dichloride, 2,2-propyl bis(9-fluorenyl)hafnium dimethyl, 2,2-propyl bis(9-fluorenyl)hafnium diethoxide, 2,2-propyl bis(1-cyclopentadienyl)hafnium dichloride, 2,2-propyl bis(1-cyclopentadienyl)hafnium dimethyl, 2,2-propyl bis(1-cyclopentadienyl)hafnium diethoxide, 2,2-propyl bis(1-indenyl)hafnium dichloride, 2,2-propyl bis(1-indenyl)hafnium dimethyl, 2,2-propyl (1-indenyl)(1-cyclopentadienyl)hafnium dimethyl, 2,2-propyl (1-indenyl)(1-cyclopentadienyl)hafnium diethoxide, 2,2-propyl bis(1-indenyl)hafnium diethoxide, 2,2-propyl (1-indenyl)(1-cyclopentadienyl)hafnium dichloride, 2,2-propyl (1-indenyl)(9-fluorenyl)hafnium dichloride, 2,2-propyl (1-indenyl)(9-fluorenyl)hafnium dimethyl, 2,2-propyl (1-indenyl)(9-fluorenyl)hafnium diethoxide, diphenylmethyl bis(1-indenyl)zirconium dibromide, diphenylmethyl bis(1-indenyl)zirconium diethyl, diphenylmethyl bis(1-indenyl)zirconium dimethoxide, diphenylmethyl bis(1-indenyl)zirconium dihydride, diphenylmethyl bis(1-indenyl)zirconium chloride bromide, diphenylmethyl bis(1-indenyl)zirconium chloride methoxide, diphenylmethyl bis(1-indenyl)zirconium chloride methyl, diphenylmethyl bis(1-indenyl)zirconium chloride hydride, diphenylmethyl (9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, diphenylmethyl (9-fluorenyl)(1-cyclopentadienyl)zirconium dimethyl, diphenylmethyl (9-fluorenyl)(1-cyclopentadienyl)zirconium diethoxide, diphenylmethyl bis(9-fluorenyl)zirconium dichloride, diphenylmethyl bis(9-fluorenyl)zirconium dimethyl, diphenylmethyl bis(9-fluorenyl)zirconium diethoxide, diphenylmethyl bis(1-cyclopentadienyl)zirconium dichloride, diphenylmethyl

bis(1-cyclopentadienyl)zirconium dimethyl, diphenylmethyl bis(1-cyclopentadienyl)zirconium diethoxide, diphenylmethyl bis(1-indenyl)zirconium dichloride, diphenylmethyl bis(1-indenyl)zirconium dimethyl, diphenylmethyl bis(1-indenyl) zirconium diethoxide, diphenylmethyl (1-indenyl)(1-cyclopentadienyl)zirconium dichloride, diphenylmethyl (1-indenyl)(1-cyclopentadienyl)zirconium dimethyl, diphenylmethyl (1-indenyl)(1-cyclopentadienyl)zirconium diethoxide, diphenylmethyl (1-indenyl)(9-fluorenyl)zirconium dichloride, diphenylmethyl (1-indenyl)(9-fluorenyl)zirconium dimethyl, diphenylmethyl (1-indenyl)(9-fluorenyl)zirconium diethoxide, diphenylmethyl (9-fluorenyl)(1-cyclopentadienyl)hafnium dichloride, diphenylmethyl (9-fluorenyl)(1-cyclopentadienyl)hafnium dimethyl, diphenylmethyl (9-fluorenyl)(1-cyclopentadienyl)hafnium diethoxide, diphenylmethyl bis(9-fluorenyl)hafnium dichloride, diphenylmethyl bis(9-fluorenyl)hafnium dimethyl, diphenylmethyl bis(9-fluorenyl)hafnium diethoxide, diphenylmethyl bis(1-cyclopentadienyl)hafnium dichloride, diphenylmethyl bis(1-cyclopentadienyl)hafnium dimethyl, diphenylmethyl bis(1-cyclopentadienyl)hafnium diethoxide, diphenylmethyl bis(1-indenyl)hafnium dichloride, diphenylmethyl bis(1-indenyl)hafnium dimethyl, diphenylmethyl bis(1-indenyl) hafnium diethoxide, diphenylmethyl (1-indenyl)(1-cyclopentadienyl)hafnium dichloride, diphenylmethyl (1-indenyl)(1-cyclopentadienyl)hafnium dimethyl, diphenylmethyl (1-indenyl)(1-cyclopentadienyl)hafnium diethoxide, diphenylmethyl (1-indenyl)(9-fluorenyl)hafnium dichloride, diphenylmethyl (1-indenyl)(9-fluorenyl)hafnium dimethyl, diphenylmethyl (1-indenyl)(9-fluorenyl)hafnium diethoxide, diphenylsilyl bis(1-indenyl)zirconium dibromide, diphenylsilyl bis(1-indenyl)zirconium diethyl, diphenylsilyl bis(1-indenyl)zirconium dimethoxide, diphenylsilyl bis(1-indenyl)zirconium dihydride, diphenylsilyl bis(1-indenyl)zirconium chloride bromide, diphenylsilyl bis(1-indenyl)zirconium chloride methoxide, diphenylsilyl bis(1-indenyl)zirconium chloride methyl, diphenylsilyl bis(1-indenyl)zirconium chloride hydride, diphenylsilyl

(9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, diphenylsilyl (9-fluorenyl)(1-cyclopentadienyl)zirconium dimethyl, diphenylsilyl (9-fluorenyl)(1-cyclopentadienyl)zirconium diethoxide, diphenylsilyl (9-fluorenyl)zirconium dichloride, diphenylsilyl (9-fluorenyl)zirconium dimethyl, diphenylsilyl (9-fluorenyl)zirconium diethoxide, diphenylsilyl (1-cyclopentadienyl)zirconium dichloride, diphenylsilyl (1-cyclopentadienyl)zirconium dimethyl, diphenylsilyl (1-cyclopentadienyl)zirconium diethoxide, diphenylsilyl (1-indenyl)zirconium dichloride, diphenylsilyl (1-indenyl)zirconium dimethyl, diphenylsilyl (1-indenyl) zirconium diethoxide, diphenylsilyl (1-indenyl)(1-cyclopentadienyl)zirconium dichloride, diphenylsilyl (1-indenyl)(1-cyclopentadienyl)zirconium dimethyl, diphenylsilyl (1-indenyl)(1-cyclopentadienyl)zirconium diethoxide, diphenylsilyl (1-indenyl)(9-fluorenyl)zirconium dichloride, diphenylsilyl (1-indenyl)(9-fluorenyl)zirconium dimethyl, diphenylsilyl (1-indenyl)(9-fluorenyl)zirconium diethoxide, diphenylsilyl (9-fluorenyl)(1-cyclopentadienyl)hafnium dichloride, diphenylsilyl (9-fluorenyl)(1-cyclopentadienyl)hafnium dimethyl, diphenylsilyl (9-fluorenyl)(1-cyclopentadienyl)hafnium diethoxide, diphenylsilyl bis(9-fluorenyl)hafnium dichloride, diphenylsilyl bis(9-fluorenyl)hafnium dimethyl, diphenylsilyl bis(9-fluorenyl)hafnium diethoxide, diphenylsilyl bis(1-cyclopentadienyl)hafnium dichloride, diphenylsilyl bis(1-cyclopentadienyl)hafnium dimethyl, diphenylsilyl bis(1-cyclopentadienyl)hafnium diethoxide, diphenylsilyl bis(1-indenyl)hafnium dichloride, diphenylsilyl bis(1-indenyl)hafnium dimethyl, diphenylsilyl bis(1-indenyl) hafnium diethoxide, diphenylsilyl bis(1-indenyl)(1-cyclopentadienyl)hafnium dichloride, diphenylsilyl bis(1-indenyl)(1-cyclopentadienyl)hafnium dimethyl, diphenylsilyl bis(1-indenyl)(1-cyclopentadienyl)hafnium diethoxide, diphenylsilyl bis(1-indenyl)(9-fluorenyl)hafnium dichloride, diphenylsilyl bis(1-indenyl)(9-fluorenyl)hafnium dimethyl, diphenylsilyl bis(1-indenyl)(9-fluorenyl)hafnium diethoxide, ethylene bis(1-indenyl)zirconium dibromide, ethylene bis(1-indenyl)zirconium diethyl, ethylene bis(1-indenyl)zirconium dimethoxide, ethylene

bis(1-indenyl)zirconium dihydride, ethylene bis(1-indenyl)zirconium chloride bromide, ethylene bis(1-indenyl)zirconium chloride methoxide, ethylene bis(1-indenyl)zirconium chloride methyl, ethylene bis(1-indenyl)zirconium chloride hydride, ethylene bis(trimethylcyclopentadienyl)zirconium dichloride, ethylene bis(5-dimethylamino-1-indenyl)zirconium dichloride, ethylene bis(6-dipropylamino-1-indenyl)zirconium dichloride, ethylene bis(4,7-bis(dimethylamino)-1-indenyl)zirconium dichloride, ethylene bis(5-diphenylphosphino-1-indenyl)zirconium dichloride, ethylene (1-dimethylamino-9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, ethylene (4-butylthio-9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, ethylene bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, ethylene bis(4-methyl-1-indenyl)zirconium dichloride, ethylene bis(5-methyl-1-indenyl)zirconium dichloride, ethylene bis(6-methyl-1-indenyl)zirconium dichloride, ethylene bis(7-methyl-1-indenyl)zirconium dichloride, ethylene bis(5-methoxy-1-indenyl)zirconium dichloride, ethylene bis(4,7-methoxy-1-indenyl)zirconium dichloride, ethylene bis(2,3-methoxy-1-indenyl)zirconium dichloride, ethylene bis(4,7-methoxy-1-indenyl)zirconium dichloride, ethylene (9-fluorenyl)(1-cyclopentadienyl)zirconium dichloride, ethylene (9-fluorenyl)(1-cyclopentadienyl)zirconium dimethyl, ethylene (9-fluorenyl)(1-cyclopentadienyl)zirconium diethoxide, ethylene bis(9-fluorenyl)zirconium dichloride, ethylene bis(9-fluorenyl)zirconium dimethyl, ethylene bis(9-fluorenyl)zirconium diethoxide, ethylene bis(1-cyclopentadienyl)zirconium dichloride, ethylene bis(1-cyclopentadienyl)zirconium dimethyl, ethylene bis(1-cyclopentadienyl)zirconium diethoxide, ethylene bis(1-indenyl)zirconium dichloride, ethylene bis(1-indenyl)zirconium dimethyl, ethylene bis(1-indenyl) zirconium diethoxide, ethylene (1-indenyl)(1-cyclopentadienyl)zirconium dichloride, ethylene (1-indenyl)(1-cyclopentadienyl)zirconium dimethyl, ethylene (1-indenyl)(1-cyclopentadienyl)zirconium diethoxide, ethylene (1-indenyl)(9-fluorenyl)zirconium dichloride, ethylene

(1-indenyl)(9-fluorenyl)zirconium dimethyl, ethylene (1-indenyl)(9-fluorenyl)zirconium diethoxide, ethylene (9-fluorenyl)(1-cyclopentadienyl)hafnium dichloride, ethylene (9-fluorenyl)(1-cyclopentadienyl)hafnium dimethyl, ethylene (9-fluorenyl)(1-cyclopentadienyl)hafnium diethoxide, ethylene bis(9-fluorenyl)hafnium dichloride, ethylene bis(9-fluorenyl)hafnium dimethyl, ethylene bis(9-fluorenyl)hafnium diethoxide, ethylene bis(1-cyclopentadienyl)hafnium dichloride, ethylene bis(1-cyclopentadienyl)hafnium dimethyl, ethylene bis(1-cyclopentadienyl)hafnium diethoxide, ethylene bis(1-indenyl)hafnium dichloride, ethylene bis(1-indenyl)hafnium dimethyl, ethylene bis(1-indenyl) hafnium diethoxide, ethylene (1-indenyl)(1-cyclopentadienyl)hafnium dichloride, ethylene (1-indenyl)(1-cyclopentadienyl)hafnium dimethyl, ethylene (1-indenyl)(1-cyclopentadienyl)hafnium diethoxide, ethylene (1-indenyl)(9-fluorenyl)hafnium dichloride, ethylene (1-indenyl)(9-fluorenyl)hafnium dimethyl, ethylene (1-indenyl)(9-fluorenyl)hafnium diethoxide.

Monocyclopentadienyl metallocene includes, for example, dimethylsilyltetramethyl cyclopentadienyl-tert-butylamido zirconium dichloride, dimethylsilyltetramethyl cyclopentadienyl-tert-butylamido hafnium dichloride, dimethylsilyltert-butylcyclopentadienyl-tert-butylamido zirconium dichloride, dimethylsilyltert-butylcyclopentadienyl-tert-butylamido hafnium dichloride, dimethylsilyltrimethylsilyl cyclopentadienyl-tert-butylamido zirconium dichloride, dimethylsilyltetramethyl cyclopentadienyl-phenylamido zirconium dichloride, dimethylsilyltetramethyl cyclopentadienyl-phenylamido hafnium dichloride, methylphenylsilyltetramethyl cyclopentadienyl-tert-butylamido zirconium dichloride, methylphenylsilyltetramethyl cyclopentadienyl-tert-butylamido hafnium dichloride, methylphenylsilyltetramethyl cyclopentadienyl-tert-butylamido zirconium dimethyl, methylphenylsilyltetramethyl cyclopentadienyl-tert-butylamido zirconium

dichloride, dimethylsilyltetramethyl cyclopentadienyl-p-n-phenylamido zirconium dichloride, dimethylsilyltetramethyl cyclopentadienyl-p-n-butylamido hafnium dichloride.

Further, the component (A) can be used in supported form, considering process limiting factors and following characteristics:

1) Shape and particle size can be controlled so that polymers having any shape and particle size can be obtained using Reprica phenomenon.

2) High bulk density of polymer can be obtained by increasing surface concentration of activated compound.

3) Collision between activated compounds is controlled so that their activity is maintained for hours and thermostability is increased whereby to improve productivity remarkably.

4) As gas phase polymerization may be conducted, manufacturing cost is decreased.

5) The catalyst may be stored for a long period of time, which makes the polymerization operation simple.

6) Heat of polymerization is easily removable by the action of carrier.

As described above, metallocene catalyst may be supported on silica, alumina or magnesium, etc., by the process of:

1) applying metallocene to Lewis' acidic alumina or magnesium chloride, then adding AlR_3 so as to form stable cation complex; or

2) fixed-supporting MAO with hydroxy group on surface of silica or alumina, then adding AlR_3 for alkylation.

can be used for supporting.

Both perchlorates and chlorates can be used as cation activators, the component (B) of the present invention.

Perchlorates are, for example, $LiClO_4$, $Ca(ClO_4)_2$, $Cd(ClO_4)_2$, $Rb(ClO_4)_2$, $Mg(ClO_4)_2$, $Pb(ClO_4)_2$, $Sr(ClO_4)_2$, $Zn(ClO_4)_2$, $Cr(ClO_4)_3$, $Mn(ClO_4)_2$, $NaClO_4$, $AgClO_4$, $Fe(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, $KClO_4$, $LiIO_4$, $Ca(IO_4)_2$, $Cd(IO_4)_2$, $Rb(IO_4)_2$, $Mg(IO_4)_2$, $Pb(IO_4)_2$, $Sr(IO_4)_2$, $Zn(IO_4)_2$, $Cr(IO_4)_3$, $Mn(IO_4)_2$, $NaIO_4$, $AgIO_4$, $Fe(IO_4)_2$, $Ni(IO_4)_2$, $Cu(IO_4)_2$, KIO_4, etc. $Mg(ClO_4)_2$ and $AgClO_4$ are most

preferable. And, hydrates of said compounds can be used.

Chlorates are, for example, $LiClO_3$, $Ca(ClO_3)_2$, $Cd(ClO_3)_2$, $Rb(ClO_3)_2$, $Mg(ClO_3)_2$, $Pb(ClO_3)_2$, $Sr(ClO_3)_2$, $Zn(ClO_3)_2$, $Cr(ClO_3)_3$, $Mn(ClO_3)_2$, $NaClO_3$, $AgClO_3$, $Fe(ClO_3)_2$, $Ni(ClO_3)_2$, $Cu(ClO_3)_2$, $KClO_3$, $LiIO_3$, $Ca(IO_3)_2$, $Cd(IO_3)_2$, $Rb(IO_3)_2$, $Mg(IO_3)_2$, $Pb(IO_3)_2$, $Sr(IO_3)_2$, $Zn(IO_3)_2$, $Cr(IO_3)_3$, $Mn(IO_3)_2$, $NaIO_3$, $AgIO_3$, $Fe(IO_3)_2$, $Ni(IO_3)_2$, $Cu(IO_3)_2$, KIO_3, etc. Hydrates of said compounds can be used as well.

Also, others such as $NH_4 \cdot ClO_4$, $Ph_3C \cdot ClO_4$, $Cl_3C \cdot ClO_4$, $NF_4 \cdot ClO_4$, $NBu_4 \cdot ClO_4$, $NH_4 \cdot IO_4$, $Ph_3C \cdot IO_4$, $Cl_3C \cdot IO_4$, $NF_4 \cdot IO_4$, $NBu_4 \cdot IO_4$ and hydrates of said compounds can be used.

All of known alkylating agents can be used as the component (C) of the present invention, however, organic metal compounds having hydrocarbyl group such as C_1-C_{20} alkyl, alkenyl, arylalkyl or allylalkyl, said metal being from IA, IIA, IIB, IIIA Group of the Periodic Table of Elements are preferable. Alkylating agents such as alkylaluminum, alkyl magnesium, alkyl zinc, etc are more preferable. For example, alkylaluminum are trimethylaluminum, triethylaluminum, triisobutylaluminum, diethylaluminum chloride, ethylaluminum sesquichloride, etc., alkyl magnesium are butyloctyl magnesium, butylethyl magnesium, dihexyl magnesium, etc., and, alkyl zinc are diethyl zinc, etc.

The catalyst system of the present invention can be prepared by contacting said components (A), (B) and (C) in any order [if component (B) / component (A) < 500, homogeneous composition is obtained, while component (B) / component (A) > 500, heterogeneous composition is obtained]. Contacting can be carried out in a known method. Generally, it is preferable to contact the components at a temperature ranging from 0 to 100℃, and the contacting time is preferably from about 10 minutes to 5 hours. Components are contacted each other under stirring. As to the contacting order, a method of processing said component (A), component (B) and component (C) simultaneously, a method of processing component (A) and component (B) and then adding component (C) thereto, and a

method of processing component (A) and component (C) and then adding component (B) thereto can be used. However, molecular weight or its distribution of produced polymer may be changed depending on contacting method or order, since active site condition of metallocene catalyst system may be changed thereby.

It is preferable to contact the components under the presence of dispersing agent. Dispersing agent such as hydrocarbon, halogenated hydrocarbon, dialkyl siloxane, etc. can be used. Hydrocarbon is, for example, hexane, heptane, toluene, cyclohexane, etc., halogenated hydrocarbon is, for example, n-butyl chloride, 1,2-dichloroethane, carbon tetrachloride, chlorobenzene, etc., and dialkyl siloxane is, for example, dimethyl polysiloxane, methyl-phenyl polysiloxane, etc.

Comonomers such as straight or branched C_3-C_{20} monoolefin, α-olefin substituted aromatic compounds, and diene compounds can be used in the preparation of copolymers of the present invention.

Examples of α-olefin are straight monoolefin such as propylene, butene-1, hexene-1, octene-1, nonene-1, decene-1, dodecene-1, hexadecene-1, icocene-1; branched monoolefin such as 3-methylbutene-1, 3-methylpentene-1, 4-methylpentene-1, 2-ethylhexene-1, 2,2,4-trimethylpentene-1; and monoolefin substituted with aromatic compound such as styrene, styrene substituted with alkyl.

Diene compounds are straight or branched non-conjugated dienes having C6-C20, for example, 1,3-butadiene, 1,4-hexadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 2-methyl-1,4-pentadiene, 2,5-dimethyl-1,5-hexadiene, 1,4-dimethyl-4-t-butyl-2,6-heptadiene, 1,5,9-decatriene, etc.

Catalyst of the present invention is efficacious for preparing olefin homopolymers and ethylene/α-olefin copolymers. For polymerization, all known methods such as solution polymerization, high temperature-high pressure polymerization, slurry polymerization, gas phase polymerization can be used. Temperature for polymerization ranges -40℃ ~ 220℃, preferably 10℃ ~ 200℃, more preferably 40℃ ~ 160℃.

By using the catalyst system according to the present invention, polyolefins having a narrow molecular weight distribution and composition distribution are obtainable. Employed at high temperature (130-160℃), the catalyst system did not accompany any problems in its activity and molecular weight of products, which were usually found in conventional catalyst system. Further, by using the catalyst system of the present invention, it is possible to lower manufacturing cost of polymers to a level when Ziegler-Natta catalyst (about 6,000-10,000won/ton PE) is used. These characteristics of the catalyst system of the present invention are advantageous for industrial use, and important considering the catalyst system itself.

Furthermore, ethylene copolymers having high molecular weight and good physical properties can be prepared with high yield, by using the catalyst system of the present invention. According to the present invention, a mixture of ethylene and C_3-C_{20} α-olefin can be polymerized in a solvent or high pressure autoclave at -40-220℃, under 1-3,000 atm such that the comonomer may be incorporated by 80wt%. Since the density of polymer to be produced is not limited by processing factors when the polymerization is carried out in a solvent or high pressure autoclave polymerization, copolymers in wide range of density (0.86-0.96g/cm^3) from VLDPE to HDPE can be synthesized.

A more complete appreciation of the present invention will be realized by reference to the following examples. The following examples are not intended to limit the invention disclosed herein but given only by way of illustration.

Example

Example 1

< Preparation of catalyst system >

0.34g(0.84mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride is placed in dried Schlenk type reactor(100ml) with magnetic bar under nitrogen atmosphere. To this reactor is added 30ml of toluene

solvent dried for about 2 hours by distillation apparatus wherein sodium/benzophenone has been added, until bis(n-butylcyclopentadienyl)zirconium dichloride is completely dissolved. Then, 0.19g (0.84mmol) of magnesium perchlorate[$Mg(ClO_4)_2$] is dropped, and the solution thus obtained is stirred for 3 hours at room temperature under nitrogen atmosphere. Pale yellow homogeneous solution of the complex produced by reaction of bis(n-butylcyclopentadienyl)zirconium dichloride and $Mg(ClO_4)_2$, which is completely dissolved in solution, is obtained. 1ml of the solution is added to another Schlenk type reactor(100ml), and diluted in 92ml of toluene for preparing catalyst solution(1).

< Ethylene polymerization >

50ml of toluene, 1ml of 1M triisobutylaluminum, and said catalyst solution(1) are added sequentially to 100ml of high pressure autoclave with magnetic bar therein under nitrogen atmosphere. Then, 5 ℓ of ethylene is introduced through the gas flow meter, and the mixture is stirred to react at 70℃ for an hour. Methanol is added to the polymer thus produced to stop the reaction, and non-reacted ethylene removed, then the polymer is added to 500ml of methanol. After a small amount of hydrochloric acid is added, and the mixture is stirred for 6 hours to remove catalysts remnant. The polymer is filtered, dried in vacuum oven at 50℃ for 8 hours to obtain 6.14g of polyethylene(see Table 1). This polymer is analysed at 145℃ with gel permeation chromatography (GPC, Waters 150C) using 1,2,4-trichlorobenzene as a solvent, and molecular weight and molecular weight distribution of polyethylene is measured(Mn=112,000, Mw=280,000, Mw/Mn=2.5 on the basis of polystyrene).

Comparative example 1

Polymerization is carried out at the same condition and with the same method as in Example 1 except that 10ml of bis(n-butylcyclopentadienyl)zirconium dichloride without cation activator is used instead of catalyst solution(1). As a Result, a very

small amount of polymer is obtained.

Comparative example 2

Polymerization is carried out at the same condition and with the same method as in Example 1 except that 0.34g(0.84mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride with 2ml(2mol) of MAO instead of cation activator is used. As a result, 4.24g of polymer is obtained. Upon GPC analysis, molecular weight and molecular weight distribution is Mn=140,000, Mw/Mn=2.1, respectively.

Example 2-8

Polymerization is carried out at the same condition and with the same method as in Example 1 except that triisobutyl aluminum(Example 2-4), trimethyl aluminum(Example 5), triethyl aluminum(Example 6), butyloctylmagnesium(Example 7) or diethyl aluminum chloride(Example 8) is used as an alkylating agent. The result is shown in Table 1.

Table 1

Example	cocatalyst	Al/Zr	polymerization activity (g-PE/mol-Zr)	Tm (℃)	△H (J/g)	Mw	Mw/Mn
1	TIBA	3300	1.5×10^{7}	132	158	280,000	2.5
2	TIBA	7	1.2×10^{4}	—	—	—	—
3	TIBA	500	9.1×10^{5}	131	162	360,000	1.8
4	TIBA	1600	1.7×10^{7}	131	161	280,000	2.0
5	TMA	3300	2.4×10^{6}	132	167	—	—
6	TEA	3300	3.6×10^{6}	—	—	480,000	2.1
7	BOM	3300	2.0×10^{5}	—	—	—	—
8	DEAC	3300	Trace	—	—	—	—

polymerization condition ; 100ml autoclave,
polymerization temperature ; 70℃,
catalyst ; (1), ethylene ; 5 ℓ, reaction time ; 1 hour
solvent ; toluene, Mg/Zr(mol/mol) ; 1

Example 9-12

Polymerization is carried out using catalyst (1) at the same condition and with the same method as in Example 1 except that cation activator is changed. The result is shown in Table 2.

Table 2

Example	cation activator	polymerization activity (g-PE/mol-Zr)	Mw	Mw/Mn
9	$AgClO_4$	4.3×10^6		
10	$AgClO_3$	2.6×10^6	—	—
4	$Mg(ClO_4)_2$	1.7×10^7	280,000	2.0
11	$Mg(IO_4)_2$	2.5×10^6	—	—
12	$Ph_3C\cdot ClO_4$	2.3×10^6	—	—

polymerization condition ; 100ml autoclave,
catalyst ; (1), cocatalyst ; TIBA(1ml, 1M solution), ethylene ; 5 ℓ,
reaction time ; 1 hour, solvent ; toluene,
Al/Zr(mol/mol) ; 1600, Mg/Metal(mol/mol) ; 1,
reaction temperature ; 70℃

Example 13-15

Polymerization is carried out using catalyst (1) at the same condition and with the same method as in Example 1 except that the concentration ratio of $Mg(ClO_4)_2$ to Zr is changed from 1 to 1000. The result is shown in Table 3.

Table 3

Example	Mg/Zr (mol/mol)	Activity (g-PE/mol-Zr)	Remarks
4	1	1.7×10^{7}	homogeneous polymerization
13	10	4.3×10^{6}	homogeneous polymerization
14	100	4.7×10^{6}	homogeneous polymerization
15	960	1.3×10^{5}	heterogeneous polymerization

polymerization condition ; 100ml autoclave,
catalyst ; (1), cocatalyst ; TIBA(1ml, 1M), ethylene ; 5 ℓ,
reaction time ; 1 hour, solvent ; toluene(50ml),
Al/Zr(mol/mol) ; 1600,
reaction temperature ; 70℃

Example 16-17

Polymerization is carried out at the same condition and with the same method as in Example 1 except that other transition metal complex is used instead of bis(n-butylcyclopentadienyl)zirconium dichloride. The result is shown in Table 4.

Table 4

Example	transition metal complex	activity (g-PE/mol-Zr)	Mw	Mw/Mn
4	$(n\text{-}BuCp)_2ZrCl_2$	1.7×10^{7}	280,000	2.0
16	CGC[a]	1.3×10^{7}	150,600	2.1
17	$rac\text{-}Et(Ind)_2ZrCl_2$	1.5×10^{7}	116,200	2.2

polymerization condition ; 100ml autoclave,
cocatalyst ; TIBA(1ml, 1M solution), ethylene ; 5 ℓ ,
reaction time ; 1 hour, polymerization temperature ; 70℃
Al/Zr(mol/mol) ; 1600, Mg/Zr(mol/mol) ; 1,
a ; (t-butylamido)dimethyl(tetramethylcyclopentadienyl)silanetitanium dichloride

Example 18-20

Polymerization is carried out at the same condition and with the same method as in Example 1 except that ethylene and hydrogen are used at the same time. The result is shown in Table 5.

Table 5

Example	H_2 (mol)	polymerization activity (g-PE/mol-Zr)	Mw	Mw/Mn
4	0	1.7×10^7	281,000	2.0
18	5	9.8×10^7	153,000	2.1
19	10	1.1×10^8	81,000	2.0
20	30	1.3×10^7	28,500	2.2

polymerization condition ; 100ml autoclave,
catalyst ; (1), cocatalyst ; TIBA(1ml, 1M solution),
ethylene ; 5 ℓ , reaction time ; 1 hour,
polymerization temperature ; 70℃
solvent ; toluene
Al/Zr(mol/mol) ; 1600, Mg/Zr(mol/mol) ; 1

Example 21-24

Polymerization is carried out using catalyst (1) at the same condition and with the same method as in Example 1 except that polymerization temperature is changed. The result is shown in Table 6.

Table 6

Example	polymerization temperature (℃)	activity (g-PE/mol-Zr)	Mw	Mw/Mn
21	40	1.3×10^7	283,000	2.2
4	70	1.7×10^7	280,000	2.0
22	100	2.3×10^7	250,000	2.1
23	140	2.5×10^7	150,000	2.0
24	160	4.0×10^5	110,000	1.8

polymerization condition ; 100ml autoclave,
catalyst ; (1), cocatalyst ; TIBA(1ml, 1M solution),
ethylene ; 5 ℓ , reaction time ; 1 hour,
solvent ; toluene.
Al/Zr(mol/mol) ; 1600, Mg/Zr(mol/mol) ; 1,

Example 25-26

Polymerization is carried out using catalyst (1) at the same condition and with the same method as in Example 1 except that various solvent is used instead of toluene. The result is shown in Table 7.

Table 7

Example	solvent	activity (g-PE/mol-Zr)	Mw	Mw/Mn
21	toluene	1.7×10^7	283,000	2.2
4	heptane	1.3×10^7	240,000	2.3
26	methylene dichloride	2.3×10^7	180,000	2.1

polymerization condition ; 100ml autoclave,
catalyst ; (1), cocatalyst ; TIBA(1ml, 1M solution),
ethylene ; 5 ℓ, reaction time ; 1 hour,
polymerization temperature ; 70℃
Al/Zr(mol/mol) ; 1600, Mg/Zr(mol/mol) ; 1

Example 27

< Preparation of catalyst >

12.1mg(0.03mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride is placed in fully dried Schlenk type reactor(100ml) with magnetic bar under nitrogen atmosphere. To this reactor is added 100ml of toluene solvent dried for about 2 hours with distillation apparatus wherein sodium/benzophenone has been added, until bis(n-butylcyclopentadienyl)zirconium dichloride is completely dissolved. Then, 6.7mg(0.03mmol) of magnesium perchlorate[$Mg(ClO_4)_2$] is dropped, and the solution thus obtained is stirred for 3 hours at room temperature under nitrogen. Pale yellow homogeneous solution of the complex produced by reaction of bis(n-butylcyclopentadienyl)zirconium dichloride and $Mg(ClO_4)_2$, which is completely dissolved in solution, is obtained. 1ml of the solution is added to another Schlenk type reactor(100ml), and diluted for preparing catalyst solution(1).

< Ethylene-propylene polymerization >

50ml of toluene, 1ml(1mmol) of triisobutylaluminum, and 1ml(0.03×10^{-2}mmol-[Zr]) of said catalyst solution(1) are added sequentially to 100ml of high pressure autoclave with magnetic bar therein under nitrogen atmosphere. Then, 0.089mol of ethylene and 0.089mol propylene are introduced quantitatively through the gas flow meter, and the mixture is reacted at 70℃. After a predetermined time, non-reacted monomer is removed, methanol is added to stop the reaction, then a large amount of methanol is added. After a small amount of hydrochloric acid is added, and the mixture is stirred for 6 hours to remove catalyst remnant. The polymer is filtered, dried in

vacuum oven at 50℃ for 8 hours to obtain ethylene/propylene copolymer of which activity is 4,500kg-polymer/mol-Zr.hr. This copolymer is analysed at 145℃ with gel permeation chromatography(GPC, Waters 150CV) using 1,2,4-trichlorobenzene as solvent, and molecular weight and distribution of molecular weight of polyethylene is measured(Mn=136,000, Mw=462,000, Mw/Mn=3.4 on the basis of polystyrene)(see Table 8).

Comparative example 3

Polymerization is carried out at the same condition and with the same method as in Example 27 except that 46.6mg(0.12mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride and 1ml(1mmol) of triisobutyl aluminum without cation activator are used instead of catalyst solution(1). As a result, a very small amount of polymer is obtained.

Comparative example 4

Polymerization is carried out at the same condition and with the same method as in Example 27 except that 2mg(0.005mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride with 1ml(3.2mmol) of MAO instead of cation activator is used. As a result, ethylene/propylene copolymer with activity being 1,400 Kg-polymer/mol-Zr.hr is obtained.

Comparative example 5

Polymerization is carried out at the same condition and with the same method as in Example 27 except that 1mg(0.0025mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride with 2mg(0.0025mmol) of dimethylanilinium tetrakis(pentafluorophenyl)boron instead of cation activator is used. As a result, ethylene/propylene copolymer of which activity is 830 Kg-polymer/mol-Zr.hr is obtained. Upon GPC analysis, molecular weight and molecular weight distribution is Mw=220,000, Mw/Mn=4.4, respectively.

Example 28-30

Polymerization is carried out at the same condition and with the same method as in Example 27 except that (pentamethylcyclopentadienyl)zirconium trichloride(Example 28), ethylene bis(1-indenyl)zirconium dichloride(Example 29), or dimethylsilyltetramethyl cyclopentadienyl-tert-butylamido titanium dichloride(CGC, Example 30) is used as a metallocene catalyst. The result is shown in Table 8a and 8b.

Table 8a

Example	catalyst	activity (kg-polymer/mol -metal. hour)	concentration of propylene in polymer (mol%)
27	$(n\text{-}BuCp)_2ZrCl_2$	4,500	8.0
28	$Me_5CpZrCl_3$	130	1.0
29	rac-$Et(Ind)_2ZrCl_2$	2,600	39.0
30	CGC	490	49.0

Table 8b

Example	Tm (℃)	ΔH (J/g)	Mw	Mw/Mn
27	105	83.7	462,000	3.4
28	125	136.5	716,000	2.9
29	40	7.7	91,000	3.4
30	No peak	-	288,000	3.3

polymerization condition ; 100ml autoclave,
polymerization temperature ; 70℃,
ethylene ; 0.089mol, $[C_2]/[C_3]=1$,
cocatalyst ; TIBA(1ml, 1M solution)
solvent ; 50ml of toluene, Mg/Metal(mol/mol) ; 1

Example 31-33

Polymerization is carried out at the same condition and with the same method as in Example 27 using catalyst of Example 27, 29 and 30 except that 1-octene is used as a comonomer instead of propylene. The result is shown in Table 9a and 9b.

Table 9a

Example	catalyst	activity (kg-polymer/mol-metal. hour)	concentration of 1-octene in polymer (mol%)
31	$(n\text{-}BuCp)_2ZrCl_2$	4,950	3.6
32	$rac\text{-}Et(Ind)_2ZrCl_2$	4,830	21.0
33	CGC	760	61.0

Table 9b

Example	Tm (℃)	ΔH (J/g)	Mw	Mw/Mn	density (g/㎤)
31	109	67.9	635,000	4.3	0.88
32	89	19.6	75,000	2.8	0.86
33	No peak	–	250,000	3.2	–

polymerization condition ; 100ml autoclave,
polymerization temperature ; 70℃,
ethylene ; 0.089mol, $[C_2]/[C_8]=1$,
cocatalyst ; TIBA(1ml, 1M solution)
solvent ; 50ml of toluene, Mg/Metal(mol/mol) ; 1

Comparative example 6

Polymerization is carried out at the same condition and with the same method as in Example 27 except that 1mg(0.0025mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride with 1ml(3.2mmol) of MAO instead of said cation activator is used. As a result, ethylene/octene copolymer of with activity being 1,140 Kg-polymer/mol-Zr.hr is obtained.

Comparative example 7

Polymerization is carried out at the same condition and with the same method as in Example 27 except that 1mg(0.0025mmol) of bis(n-butylcyclopentadienyl)zirconium dichloride with 2mg(0.0025mmol) of dimethylanilinium tetrakis(pentafluorophenyl)boron instead of said cation activator is used. As a result, ethylene/octene copolymer with activity being 1,160 Kg-polymer/mol-Zr.hr is obtained. Upon GPC analysis, molecular weight and molecular weight distribution is Mw=382,000, Mw/Mn=3.4, respectively.

Example 34-36

Polymerization is carried out using ethylene bis(1-indenyl)zirconium dichloride used in Example 29 at the same condition and with the same method as in Example 27 except that polymerization temperature is changed. The result is shown in Table 10a and 10b.

Table 10a

Example	polymerization temperature	activity (kg-polymer/mol-metal . hour)	concentration of propylene in polymer (mol%)
29	70	2,600	39
34	107	21,500	–
35	160	78,100	–
36	180	85,400	26

Table 10b

Example	Tm (℃)	△H (J/g)	Mw	Mw/Mn
29	40.0	7.7	91,000	3.4
34	104.7	12.7	83,000	3.1
35	111.0	20.6	53,000	3.2
36	114.3	19.6	51,000	3.6

polymerization condition ; 100ml autoclave,
ethylene ; 0.089mol, $[C_2]/[C_8]=1$, solvent ; 50ml of toluene,
cocatalyst ; TIBA(1ml, 1M solution),
Mg/Metal(mol/mol) ; 1

What is claimed is:

1. A catalyst system for olefin polymerization and copolymerization comprising (A) at least one metallocene compound derived from a transition metal, (B) at least one cation activator as cocatalyst, and (C) at least one alkylating agent.

2. The catalyst system according to claim 1, wherein said cation activator is represented by the formula:

$$M^{n+}(X^-)_{n-g}Z_g$$

wherein,

$n = 1, 2, 3$ or 4, and g is an integer such that $0 \leq g < n$;

M is a metal from Group IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIIIB, IB or IIB of the Periodic Table of Elements, or an organic compound;

X is an anion cluster comprising more than three elements, wherein one or more element is selected from the group consisting of O, S, N, F, Cl, Br and I; and

Z is H^-, or F, Cl, Br or I.

3. The catalyst system according to claim 2, wherein said cation activator (B) reacts with said metallocene transition metal complex (A) to form cation of said metallocene transition metal by X^- anion having very weak coordination bonding force whereby to induces olefin polymerization activity.

4. The catalyst system according to claim 3, wherein said X is one or more perchlorate anion, and M is selected from Li, Na, Ca, Mg or Ag.

5. The catalyst system according to claim 4, wherein said cation activator (B) is selected from $LiClO_4$, $NaClO_4$, $Ca(ClO_4)_2$, $Mg(ClO_4)_2$ or $AgClO_4$.

6. The catalyst system according to claim 2, wherein said X is one or more perchlorate anion, and M is an organic compound containing either C or N.

7. The catalyst system according to claim 6, wherein said cation activator (B) is selected from $NH_4 \cdot ClO_4$, $Ph_3C \cdot ClO_4$, $Cl_3C \cdot ClO_4$, $NF_4 \cdot ClO_4$, $NBu_4 \cdot ClO_4$.

8. The catalyst system according to claim 1, wherein said alkylating

agent (C) is an organometallic compound having hydrocarbyl group such as C_1-C_{20} alkyl, alkenyl, arylalkyl or allylalkyl, wherein said metal is selected from IA, IIA, IIB, IIIA Groups of the Periodic Table of Elements.

9. The catalyst system according to claim 8, wherein said alkylating agent (C) is alkyl aluminum, alkyl magnesium or alkyl zinc.

10. The catalyst system according to claim 9, wherein said alkylating agent (C) is selected from alkyl aluminum, alkyl magnesium or alkyl zinc such as trimethyl aluminum, triethyl aluminum, triisobutyl aluminum, diethyl aluminum chloride, ethyl aluminum sesquichloride, butyl octyl magnesium, butyl ethyl magnesium, dihexyl magnesium or diethyl zinc.

11. The catalyst system according to claim 1, wherein the molar ratio of (A) to (B) is 1:0.01 ~ 100, and (A) to (C) is 1: 1 ~ 10,000.

12. The catalyst system according to claim 1, wherein the molar ratio of (A) to (B) is 1:0.01 ~ 10, and (A) to (C) is 1: 100 ~ 2,000.

13. The catalyst system according to claim 11, wherein the molar ratio of (A) to (B) is 1:1, and (A) to (C) is 1: 100 ~ 2,000.

14. A process for preparing olefin homopolymers using the catalyst system according to any one of claims 1 to 13.

15. The process according to claim 14, wherein said olefin is ethylene.

16. The process according to claim 14, wherein said polymers are prepared by solution polymerization, high temperature-high pressure polymerization, slurry polymerization or gas phase polymerization.

17. A process for preparing copolymer of ethylene and α-olefin using the catalyst system according to any one of claims 1 to 13.

18. The process according to claim 17, wherein said α-olefin is the one substituted with straight or branched C_3-C_{20} monoolefin or aromatic groups, or straight or branched non-conjugated C_6-C_{20} diene.

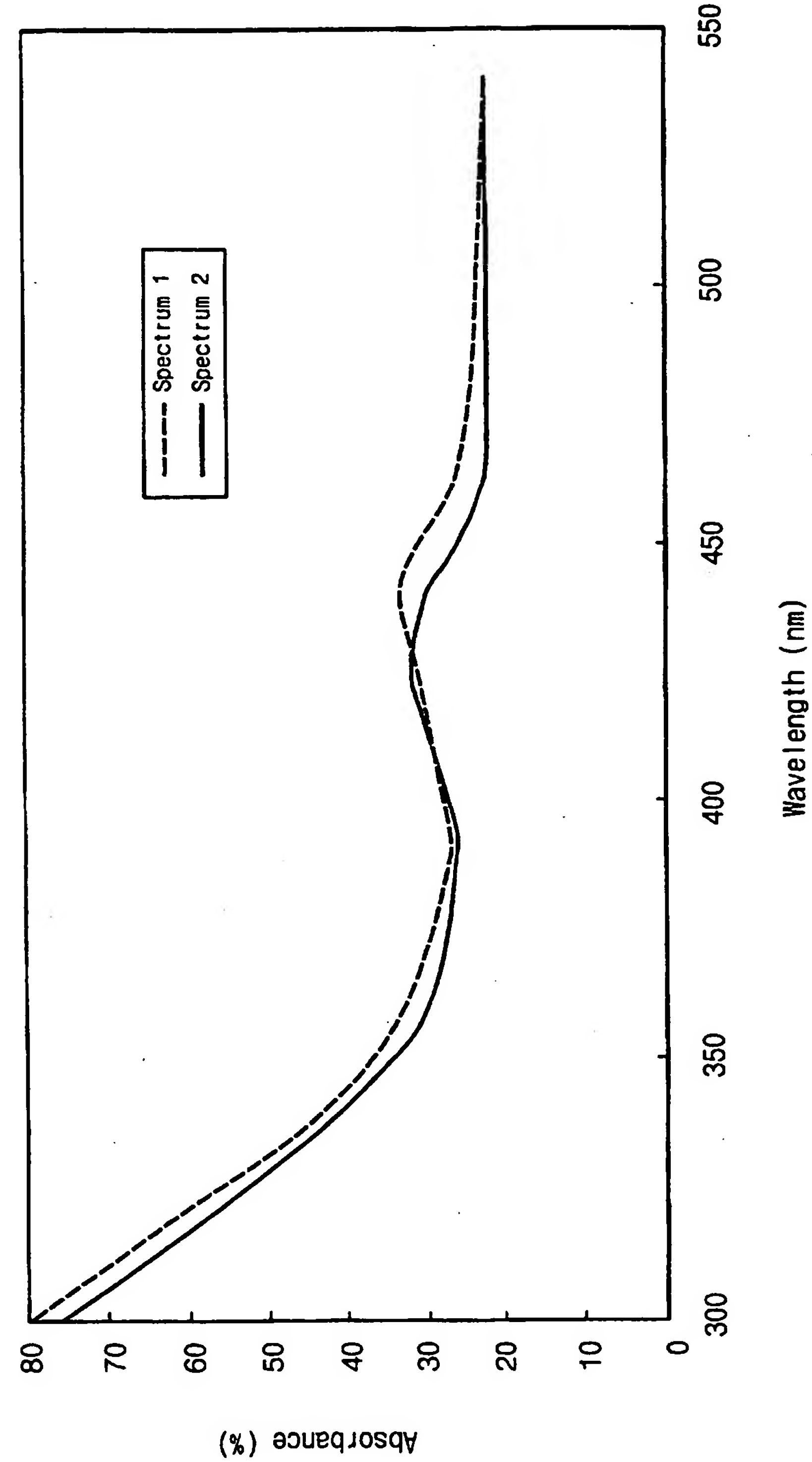
19. The process according to claim 18, wherein said α-olefin is propylene, butene-1, hexene-1, octene-1, nonene-1, decene-1, dodecene-1, hexadecene-1 or icosene-1.

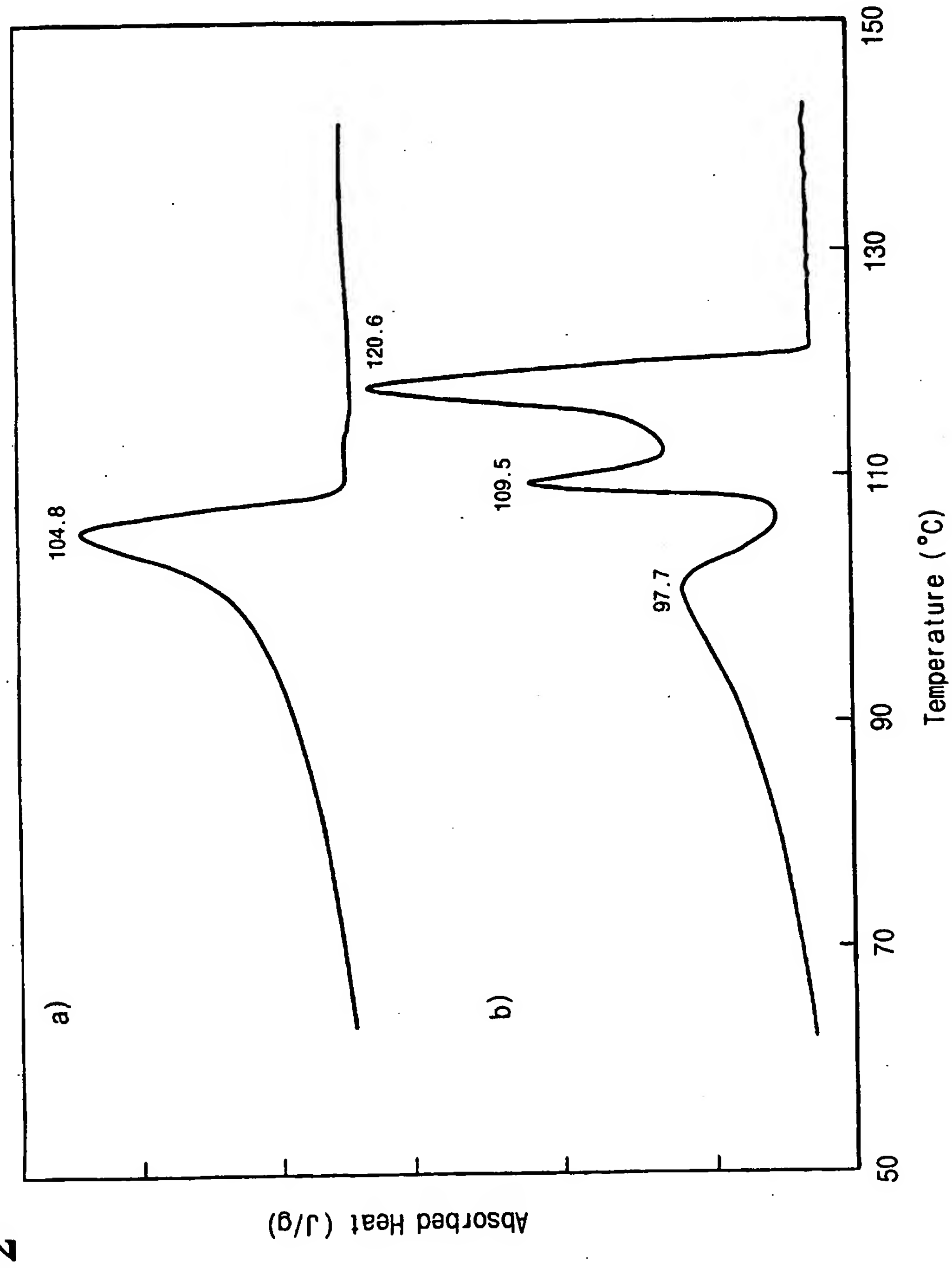
20. The process according to claim 18, wherein said α-olefin is styrene.

21. The process according to claim 18, wherein said diene is 1,3-butadiene, 1,4-hexadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 2-methyl-1,4-pentadiene, 2,5-dimethyl-1,5-hexadiene, 1,4-dimethyl-4-t-butyl-2,6-heptadiene, or 1,5,9-decatriene

22. The process according to any one of claims 17 to 21, wherein said polymers are prepared by solution polymerization, high temperature-high pressure polymerization, slurry polymerization or gas phase polymerization carried out at temperature of -40～220℃, under pressure of 1～3,000atm.

FIG. 1


Spectrum 1
Spectrum 2
Absorbance (%)
Wavelength (nm)
0
10
20
30
40
50
60
70
80
300
350
400
450
500
550



a)
b)
104.8
120.6
109.5
97.7
Absorbed Heat (J/g)
Temperature (°C)
50
70
90
110
130
150

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No. PCT/KR 97/00164

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C 08 F 4/642, 10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C 08 F 4/00, 10/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 590 486 A2 (IDEMITSU KOSAN COMPANY LIMITED) 06 April 1994 (06.04.94), abstract; page 5, line 45; page 6, line 52; page 8, lines 1-26; page 9, lines 50-58.	1-22
X	EP 0 582 268 A2 (TOSOH CORPORATION) 09 February 1994 (09.02.94), abstract; examples.	1,2,9-22

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 November 1997 (18.11.97)	26 November 1997 (26.11.97)

Name and mailing address of the ISA/ AT	Authorized officer
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